

Spectrophotometric Characterization of Some Doped Pr(III) Systems with O, N and S Containing Ligands

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The present paper is concerned with studies on electronic spectral parameters, viz., Judd Ofelt parameters (T_λ), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and symmetry parameter (T_4/T_6). These parameters are evaluated for doped Pr(III) ion with various organic reagents having O, N and S as donor atoms in M-L interaction and the change in symmetry around Pr(III) ion is discussed.

Key Words: Electronic spectral parameters, Doped Pr(III) system.

INTRODUCTION

Lanthanides are known to form complexes less readily due to deeply buried *f*-orbitals, but their bonding tendency with various types of ligands is also found in literature^{1,2}. Synthesis of sulphonanilides of salicylic acid, methyl salicylate and ethyl salicylate was carried out by employing the steps as mentioned in literature³⁻⁷.

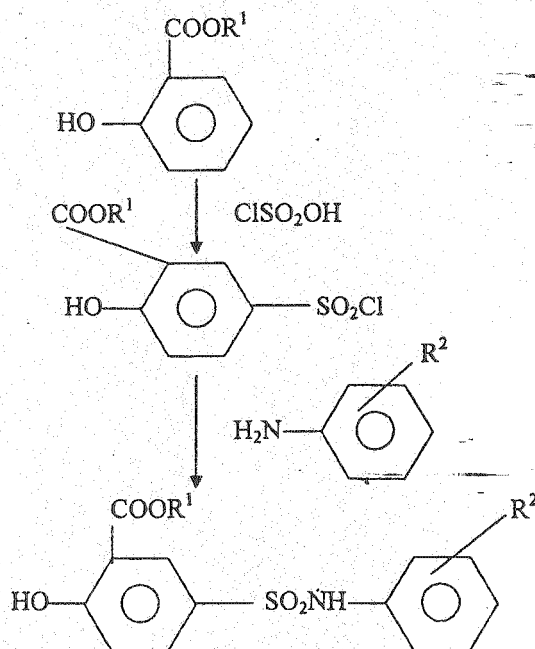
Sulphonanilides have oxygen, nitrogen and sulphur as donor atoms available for interaction with lanthanides; so different sulphonanilides (Table-1) have been taken as ligands for the formation of complexes with Pr(III) ion and their complexation behaviour was established by electronic spectral parameters such as Judd Ofelt intensity parameter (T_2 , T_4 and T_6), nephelauxetic ratio (β), bonding parameters ($b^{1/2}$) and symmetry parameter (T_4/T_6) etc.

EXPERIMENTAL

Nine sulphonanilide ligands have been synthesized in two steps according to literature³⁻⁷.

TABLE-1

Ligand No.	Groups and their position	
	R ¹	R ²
L ₁	H	<i>o</i> -NO ₂
L ₂	H	<i>m</i> -NO ₂
L ₃	H	<i>p</i> -NO ₂
L ₄	CH ₃	<i>o</i> -NO ₂
L ₅	CH ₃	<i>m</i> -NO ₂
L ₆	CH ₃	<i>p</i> -NO ₂
L ₇	C ₂ H ₅	<i>o</i> -NO ₂
L ₈	C ₂ H ₅	<i>m</i> -NO ₂
L ₉	C ₂ H ₅	<i>p</i> -NO ₂



Synthesis of Systems

Nine systems were prepared by using $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ and ligands L_1 to L_9 in 1 : 2 molar ratio (modified doped model) in DMF medium. Solution spectra were recorded for Pr(III)-ligand systems in the range of 400–625 nm by using standard spectrophotometer (Systronics 106).

RESULTS AND DISCUSSION

Values of various electronic spectral parameters are presented in Tables 2–5. All the systems have been classified into three categories on the basis of symmetry parameter values:

Category A: Pr(III)- L_7 and Pr(III)- L_8

Category B: Pr(III)- L_5 and Pr(III)- L_9

Category C: Pr(III)- L_1 , Pr(III)- L_2 , Pr(III)- L_3 , Pr(III)- L_4 , Pr(III)- L_6

The three categories *viz.*, A, B and C have the symmetry parameter values (T_4/T_6 ratio) ranging from 0.23–0.28, 0.29–0.34 and 0.35–0.40 respectively. Each category corresponds to a different stereo-environment around lanthanide ion, *i.e.*, the changed coordination behaviour.

The average values of nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) have been found to be 0.9905 and 0.0686 respectively. Nephelauxetic ratio ($\beta < 1$) and positive value of bonding parameter ($b^{1/2}$) (Table-6) infers covalency in metal ligand bonding.

The value of oscillator strength for bands have been found to be 4.24–43.7 and these values were recalculated by using computed values of Judd Ofelt parameters (T_λ). A close agreement between observed and calculated values of oscillator strength have been found which establishes the validity of Judd Ofelt equation. The metal-ligand interaction was also observed as there was increase in intensity of hypersensitive band ($^3\text{H}_4 \rightarrow ^3\text{P}_2$).

TABLE-2
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH (P) OF THE BANDS RECORDED FOR Pr(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

Pr(III) ion systems involving ligand environment (1 : 2 molar ratio) in DMF solvent									
S.No.	Levels	Free Pr(III)ion		Pr(III) with L ₁		Pr(III) with L ₂		Pr(III) with L ₃	
		$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$	$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$	$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$	$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$
1.	³ P ₂	24.6	24.6	43.7	43.7	38.0	38.0	41.7	41.7
2.	³ P ₁	10.3	10.3	16.9	16.9	16.3	16.3	16.8	16.8
3.	³ P ₀	6.25	6.25	17.2	17.2	15.3	15.3	17.0	17.0
4.	¹ D ₂	5.08	5.08	10.3	10.3	8.80	8.80	9.78	9.78
r.m.s. dev.		$\pm 9.19 \times 10^{-7}$		$\pm 2.53 \times 10^{-9}$		$\pm 2.24 \times 10^{-9}$		$\pm 2.48 \times 10^{-9}$	

TABLE-3
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH (P) OF THE BANDS RECORDED FOR Pr(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

Pr(III) ion systems involving ligand environment (1 : 2 molar ratio) in DMF solvent							
S.No.	Levels	Pr(III) with L ₄		Pr(III) with L ₅		Pr(III) with L ₆	
		$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$	$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$	$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$
1.	³ P ₂	36.1	36.1	32.5	32.5	34.7	34.7
2.	³ P ₁	14.4	14.4	11.9	11.9	13.7	13.7
3.	³ P ₀	14.4	14.4	11.0	11.0	12.9	12.9
4.	¹ D ₂	10.4	10.4	8.82	8.82	9.87	9.87
r.m.s. dev.		$\pm 2.10 \times 10^{-8}$		$\pm 1.61 \times 10^{-8}$		$\pm 1.89 \times 10^{-8}$	

TABLE-4
OBSERVED AND CALCULATED VALUES OF OSCILLATOR STRENGTH (P) OF THE BANDS RECORDED FOR Pr(III) ION SYSTEMS INVOLVING LIGAND ENVIRONMENT IN DMF SOLVENT

Pr(III) ion systems involving ligand environment (1 : 2 molar ratio) in DMF solvent							
S.No.	Levels	Pr(III) with L ₇		Pr(III) with L ₈		Pr(III) with L ₉	
		$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$	$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$	$P_{\text{obs}} \times 10^6$	$P_{\text{cal}} \times 10^6$
1.	³ P ₂	42.5	42.5	27.6	27.6	29.3	29.3
2.	³ P ₁	11.5	11.5	9.66	9.66	10.3	10.3
3.	³ P ₀	13.2	13.3	5.75	5.75	9.10	9.10
4.	¹ D ₂	8.02	8.02	4.24	4.24	5.08	5.08
r.m.s. dev.		$\pm 1.94 \times 10^{-8}$		$\pm 8.42 \times 10^{-8}$		$\pm 1.33 \times 10^{-8}$	

TABLE-5
COMPUTED VALUES OF T_λ PARAMETERS FOR Pr(III) ION SYSTEMS INVOLVING
LIGAND ENVIRONMENT IN DMF SOLVENT

S.No.	Pr(III) System	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$	T_4/T_6
1.	Free Pr(III) ion	-50.0	2.30	7.27	0.31
2.	Pr(III)-L ₁	-60.7	4.83	13.3	0.36
3.	Pr(III)-L ₂	-58.2	4.31	11.5	0.37
4.	Pr(III)-L ₃	-59.1	4.75	12.7	0.38
5.	Pr(III)-L ₄	-8.45	4.04	10.9	0.37
6.	Pr(III)-L ₅	-19.8	3.21	9.93	0.32
7.	Pr(III)-L ₆	-10.4	3.73	10.5	0.35
8.	Pr(III)-L ₇	-10.4	3.47	13.1	0.26
9.	Pr(III)-L ₈	-88.8	2.14	8.51	0.25
10.	Pr(III)-L ₉	-81.8	2.71	8.95	0.30

TABLE-6
COMPUTED VALUES OF β AND $b^{1/2}$ FOR Pr(III) SYSTEMS

S.No.	Band	Average energy [in cm^{-1}]	β	$b^{1/2}$
1.	³ P ₂	22222.22	0.9889	0.0744
2.	³ P ₁	21067.77	0.9923	0.0620
3.	³ P ₀	20455.55	0.9920	0.0632
4.	¹ D ₂	16898.88	0.9888	0.0748
	Mean		0.9905	0.0686

Free ion values for different bands of Pr(III) ion. For ³P₂ band: 22470 cm^{-1} , ³P₁ band: 21230 cm^{-1} , ³P₀ band: 20620 cm^{-1} , ¹D₂ band: 17090 cm^{-1} .

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